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افزایش بازده در سلول‌های خورشیدی پروسکایتی با اضافه‌کردن لیتیوم فلوراید به لایه انتقال‌دهنده الکترون

دارکو عبدالله نوری[الف‌وب]، عباس بهجت[الف‌وب]، مسعود دهقانی‌پور[الف‌وب] ، و علی بنویدی[ج]

[الف] گروه اتمی و مولکولی، دانشکده فیزیک، دانشگاه یزد، یزد، ایران

[ب] گروه تحقیقاتی فوتونیک، دانشگاه یزد، یزد، ایران

[ج]دانشکده شیمی، دانشگاه یزد، یزد، ایران

چکیده- اخیراً سلول‌های خورشیدی پروسکایتی به عنوان نسل سوم سلول‌های خورشیدی برپایه مواد پروسکایتی ظهور کرده‌اند. مواد پروسکایتی خواصی از قبیل هزینه کم، قابلیت تنظیم گاف انرژی، ساخت آسان، امکان ساخت در زیرلایه‌های مختلف و کارایی بالا دارند. تیتانیوم دی‌اکسید ($TiO_۲$) به عنوان یک گزینه مناسب برای لایه انتقال دهنده الکترون در سلول‌های خورشیدی پروسکایتی می‌باشد. در تحقیق حاضر، لیتیوم فلوراید (LiF) به عنوان دوپینگ برای بهبود خواص الکتریکی لایه انتقال دهنده الکترون و کارآیی پروسکایت بکار گرفته شد. نتایج نشان داد که دوپه کردن LiF رسانندگی $TiO_۲$ را افزایش می‌دهد، بازترکیب الکترون-حفره را سرکوب و خواص کریستالی لایه پروسکایت را بهبود می‌بخشد. با اصلاح لایه ETL، کارآیی سلول‌های خورشیدی پروسکایتی بدون لایه انتقال دهنده حفره ۴۸٪ افزایش پیدا کرد و منجر به ساخت سلول‌هایی با بازده ماکزیمم ۹/۳۳٪ شد.

کلید واژه- لیتیوم فلوراید، سلول‌های خورشیدی پروسکایتی، بازده تبدیل انرژی، تیتانیوم دی‌اکسید، لایه انتقال دهنده الکترون.

Efficiency Enhancement in Perovskite Solar Cells by Doping Lithium Fluoride in Electron Transporting Layer

Darko A. Noori [a,b,†], A. Behjat [a,b], M. Dehghanipour [a,b] , and A. Benvidi [c]

[a]Atomic and Molecular Group, Faculty of Physics, Yazd University, Yazd, Iran

[b] Photonics Research Group, Yazd University, Yazd, Iran

[c] Faculty of Chemistry, Yazd University, Yazd, Iran

[†] Corresponding author: darko.abdullah@gmail.com

Abstract- Recently, adopted perovskite solar cells (PSCs) as the third generation of solar cells based on perovskite materials ($ABX_۳$). PSCs have their unique properties, such as low-cost, band-gap tunability, simple fabrication, the opportunity of substrates, and high performance. Titanium dioxide ($TiO_۲$) is an attractive choice for the electron transporting layer (ETL) in PSCs. In the current study, lithium fluoride (LiF) dopant was used to enhance electrical properties of the (ETL) and perovskite performance. The results showed that LiF-doping increased the conductivity of $TiO_۲$, suppressed electron-hole recombination at ETL/perovskite interface, and improved crystallinity properties of the perovskite layer. Through ETL modification, the performance of PSCs without hole transporting layer (HTL) ۴۸٪ improved and endowed the devices with a champion power conversion efficiency of ۹,۳۳٪.

Keywords: Lithium fluoride, Perovskite solar cells, Power conversion efficiency, Titanium dioxide, Electron transport layer.

۱. Introduction

Requires to energy is truly important for life's continuity. Sun as renewable energy is the major source of our humanity's life for heat and light on Earth's surface. The light energy source can convert to electrical energy by using solar cell devices, this process is called the PV effect [۱].

Solar cells are usually classified by first, second, and third generations. First-generation solar cell based on silicon semiconductor as a single silicon crystal (mono-crystalline), many crystals (poly-crystalline), and sometimes amorphous silicon. Second generation cells are thin-film solar cells and yet based on a p-n junction design. These include gallium arsenide (GaAs) and amorphous silicon (a-Si: H), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) cells [۲]. Currently, third-generation solar cells are produced comprising several thin-film technologies often defined as emerging photovoltaics, third-generation includes dye-sensitized solar cells (DSCs), organic photovoltaics (OPVs), quantum dot solar cells (QDSCs), and perovskite solar cells (PSCs) [۳].

Recently, researchers work on the PSCs, because of its one of the suitable manufactured type's solar cells. PSCs rapidly enhanced efficiency; that is PCE increased from ۳,۸٪ to ۲٥,٥٪ during the last decade years [٤]. A perovskite structure is any compound that allows a cubic structure in the general formula ($ABX_{۳}$) [٥], where A and B are cations (A is larger than B) and X is a halogen anion. While the ETL shows a crucial part in obtaining and transporting photo-generated electron carriers and serves as a hole blocking layer by suppressing charge recombination as one of the most powerful pieces for PV devices [٦].

In general, $TiO_{۲}$ is used as ETL in PSCs due to its properties such as suitable energy level respect with to perovskite layer, fast electron mobility injection rates, good transparency, but have low electron mobility. In this study, LiF was doped in mp-$TiO_{۲}$ for enhancement of the efficiency of the PSCs.

۲. Experimental

۲,۱. Materials Preparations

Lead iodide ($PbI_{۲}$) and methylammonium iodide (MAI) were synthesised as reported in the [۷], dimethylformamide (DMF, ۹۹٪ Merck), dimethyl sulfoxide (DMSO, ۹۹٪ EXIR), chlorobenzene (CB, ۹۹,۵٪ □□□□), □□□□□□□ (□۲□۵□□, ۹۹,۵٪ □□□□□), acetone ($C_{۳}H_{٦}O$, ۹۹٪ Merck), isopropyl alcohol (IPA, $C_{۳}H_{۸}O$, ۹۸٪), hydrochloric acid (HCl ۲M), titanium isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$, ۹۸٪ EXIR), paste-$TiO_{۲}$ (۲۰ nm, Sharif Solar), lithium fluoride (LiF, ۹۹,۹۸٪ Alfa Aesar), glass substrates, pre-coated with a central fluorine-doped tin oxide (FTO) stripe. A $MAPbI_{۳}$ precursor solution was made through dissolving ٤٦۲ mg $PbI_{۲}$ and ۱٥۹ mg MAI in DMSO: DMF (۱:۹, v/v) solvent and stirred for ۳۰ minutes at ٦۰ °C. The mp-$TiO_{۲}$ precursor was formed by dissolving paste $TiO_{۲}$ in ethanol solvent (۱:٥, w/w) and stirred for ۲٤ hours at room temperature (RT). The LiF solution was prepared by dissolving ٦ mg LiF in ۳ mL ethanol and stirred at RT for ۱ hour.

۲,۲. Solar cells fabrication

Pre-patterned FTO coated glasses were sequentially cleaned with DI water, acetone, ethanol, and isopropanol under ultra-sonication for ۱٥ minutes each. The compact $TiO_{۲}$ (c-$TiO_{۲}$) solution was filtered through a ۰,۲۰ µm syringe filter and spin-coated onto FTO substrate at ٤۰۰۰ rpm for ۶۰ □□□□□□□, □□□□ □□□ □-□□□۲ □□□□ □□□ □□□□□□□□ □□ ۵۰۰ □□ □□□ ۶۰ □□□. □□-□□□۲ □□□□□□□□□□ □□□□

various amounts of LiF dopant (٠-٧,٥٪ in v/v) were spin-coated at ٤٠٠٠ rpm for ٦٠ seconds, then annealed at ٥٠٠ °C for ٩٠ min. After cooling at RT, perovskite precursor spin-coated with ٤٠٠٠ rpm for ۵۰ □□□□□□□, □□□□□□□ □□□□–□□□□□□□ (□□) □□□ □□□□□□□.
The perovskite films were then annealed for ٣٠ min at ١٠٠ °C. Finally, ٧٠ nm of the gold top electrode were sputtered under a high vacuum.

٣. Results and Discussions

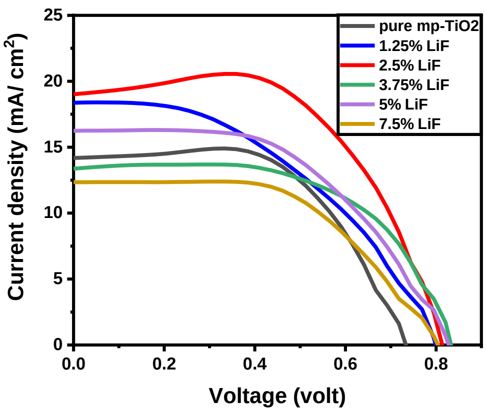

Fig. ١: J-V characteristics of PSC for different volume ratios LiF-TiO٢ as the electron transport layer.

LiF with a volume ratio (v/v) of ١,٢٥٪, ٢,٥٪, ٣,٧٥٪ and ٥٪ was doped into mp-TiO٢, and used as ETL to fabricate HTL-free PSCs. Presented that the LiF dopant to mp-TiO٢ layer affects the PV performance, electrical and optical properties of the PSCs. Solar cell performance was measured under (simulated illumination, AM ١,٥). Fig. ١ shows J-V characteristics of PSCs for different volume ratios of LiF-TiO٢. PCE enhanced from ٦,٢٩٪ (with maximum current density *Jsc* of *14.18 mA/cm²*, for pure mp-TiO٢) to ٩,٣٣٪ (with *Jsc* of *19.02 mA/cm²*, for ٢,٥٪ LiF doped mp-TiO٢), see Table I. Considering LiF-dopant inducts, the conduction energy band became higher than the pure TiO٢, it meaning that a band alignment happened between the ETL and perovskite layer.

Fig.٢ illustrates the conductivity of the doped ETL layer ($\sigma = ۱.۴۴ \times ۱۰^{-۳}\, mS.cm^{-۱}$) was increased by compared with undoped mp-TiO٢ ($\sigma = ۱.۲۰ \times ۱۰^{-۳}\, mS.cm^{-۱}$).

The optical transmittance of ETL layers with ٢,٥٪ and without the LiF dopant was studied in Fig.٣. It shows that the LiF dopant does not have a series negative effect on the transmittance of the ETL layer, and light can harvest by the perovskite layer to generate electron-hole carriers with no intense losses within ETL.

Table I. Photovoltaic parameters performance of PSC with LiF-TiO٢ as the electron transport layer.

LiF doped (v %)	Efficiency (%)		V_{oc} (v)	J_{sc} (mA/cm۲)	Fill Factor
	Max.	Ave.			
۰	۶,۲۹	۵,۳۷	۰,۷۳	۱۴,۱۸	۰,۶۰
۱,۲۵	۶,۵۰	۵,۸۶	۰,۸۱	۱۸,۳۷	۰,۴۴
۲,۵۰	۹,۳۳	۷,۵۵	۰,۸۱	۱۹,۰۲	۰,۶۱
۳,۷۵	۶,۶۸	۶,۰۳	۰,۸۳	۱۳,۳۷	۰,۶۰
۵,۰۰	۶,۶۳	۵,۶۶	۰,۸۳	۱۶,۲۴	۰,۵۲
۷,۵۰	۵,۵۲	۵,۲۸	۰,۸۱	۱۲,۳۴	۰,۵۵

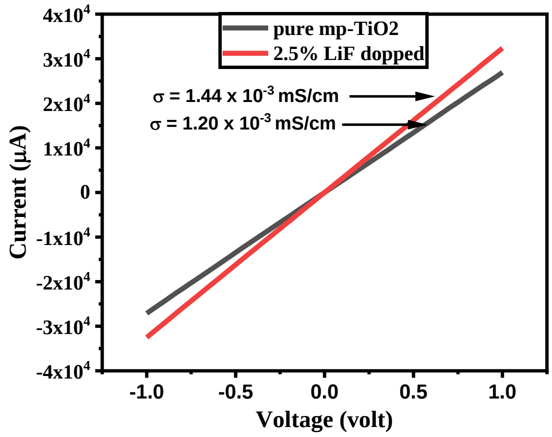

Fig. ٢: I-V measurements of pure mp-TiO٢ and LiF doped to mp-TiO٢, the thickness of the mesoporous layer was (٢٠٠ nm), and the area was (٤٥ mm٢).

The effect of LiF-doping on the crystallinity of the perovskite layer is confirmed by PL intensity and XRD as shown in Figs. ٤a and ٤b. The peak's intensity of (١١٠) plane diffraction of LiF-doped TiO٢ increased, which means well crystallization. Notably, there was no observed shift in XRD peaks position, suggesting that the LiF dopant in ETL does not diffuse into the perovskite layer. With the addition of LiF dopant into the ETL, the intensity of PL peak reduced, which refers to lower charge recombination at the interface of ETL/perovskite. In addition, a light blue shift was observed in the PL response of PSCs with LiF-doped ETL. It indicates ETL modification reduces band-tail state in the corresponding perovskite layer. The reduced charge recombination at ETL/perovskite, improved conductivity, and better crystallinity of perovskite layer in the LiF-doped based PSCs, altogether led to a performance improvement in PSCs.

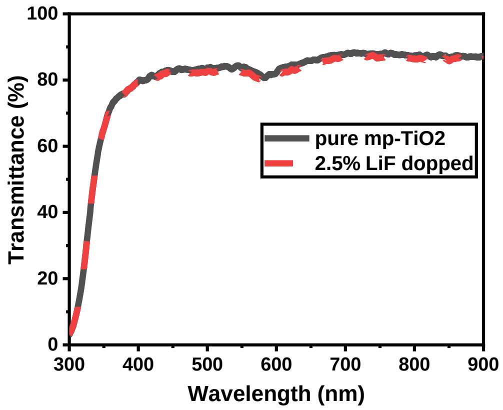

Fig. ۳: Transmittance spectra of electron transport layer for pure and doped mp-TiO_2.

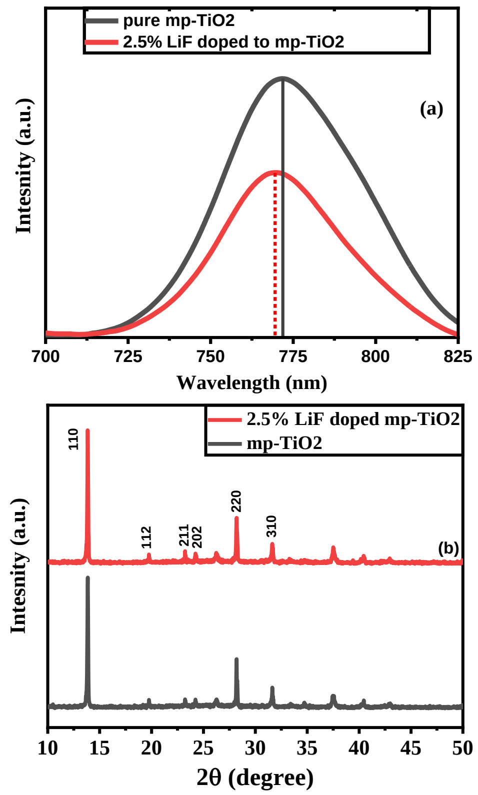

Fig. ٤: (a) PL characteristics and (b) XRD patterns of perovskite films on pure and LiF-doped TiO_2.

Acknowledgments

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